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Key Points:

- Nutrient availability (N:P) to characterize DMS and isoprene in Atlantic Ocean
- Mesoscale eddies have an effect on the DMS and isoprene distribution
- DMS and isoprene have common sources in the surface ocean

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Nutrient availability determines dimethyl sulfide and isoprene distribution in the eastern Atlantic Ocean

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Abstract Continuous high-resolution underway measurements of dimethyl sulfide (DMS) and isoprene in the ocean surface were conducted from Germany to South Africa in November 2008. DMS, total dimethylsulfoniopropionate (DMSP_T), isoprene and 19'-hexanoyloxyfucoxanthin (19'-hex) correlated in nitrogen-depleted regions when they were clustered by nitrogen to phosphorous ratio (N:P). The 19'-hex-containing algae groups might be a common source of DMS, DMSP_T, and isoprene in the low N:P regions. Additionally, DMS and isoprene correlated in nitrate-depleted regions when they were clustered against nitrate concentrations. Correlations between DMS and isoprene were also found within nitrate-depleted eddies encountered along the cruise track. Eddies with N:P of ~2.8 showed the highest positive correlations between DMS and isoprene. We conclude that the DMS/isoprene relationships in the eastern Atlantic Ocean were influenced by nutrient availability, with implications for using nutrients to predict the DMS and isoprene concentrations over a range of oceanographic areas depleted in nitrogen.

1. Introduction

Dimethyl sulfide (DMS) and isoprene (2-methyl-1,3-butadiene) are atmospheric trace constituents, which have been shown to play important roles in atmospheric chemistry and Earth's climate. DMS emitted from the ocean is a major precursor of sulfate aerosols in the marine atmosphere, which could form cloud condensation nuclei (CCN) and thus affect cloud formation [Vogt and Liss, 2009]. Additionally, DMS also contributes to upper tropospheric sulfur loading in tropical regions [Marandino et al., 2013]. However, Quinn and Bates [2011] doubt the overarching control of DMS on CCN formation and suggested alternative CCN precursors, such as nonvolatile organic compounds or sea-salt particles.

Isoprene is the most abundant biogenic nonmethane hydrocarbon in the atmosphere. Its oxidation products can form secondary organic aerosols [Schmitt-Kopplin et al., 2012] and thus indirectly impact Earth's climate [Shaw et al., 2010]. Additionally, isoprene affects the balance of oxidants in the atmosphere and plays a key role in the formation and destruction of tropospheric ozone [Houweling et al., 1998]. Terrestrial vegetation is the largest source of isoprene to the atmosphere [Sharkey et al., 2008, and references therein], while the ocean is a comparably weak source [Baker et al., 2000; Arnold et al., 2009]. However, oceanic isoprene emissions may have important seasonal and/or regional impacts, especially in productive areas of remote marine regions and coastal upwelling areas, because isoprene is highly volatile and reactive [Shaw et al., 2010].

Phytoplankton plays a central role in the oceanic pathways of both gases. Dimethylsulfoniopropionate (DMSP), the major precursor of DMS, is formed by phytoplankton and can be cleaved to DMS by bacteria and phytoplankton. Furthermore, DMS can be consumed by bacteria, oxidized photochemically, and can be emitted to the atmosphere [Stefels et al., 2007; Vogt and Liss, 2009]. In contrast, comparably little is known about the oceanic pathways of isoprene. A wide range of phytoplankton species of different functional groups, as well as seaweed, can produce isoprene [Shaw et al., 2010; Exton et al., 2013]. Kuzma et al. [1995] observed isoprene production by bacteria on land; thus, it seems likely that marine bacteria may also produce isoprene. Less is known about the chemical loss of oceanic isoprene, and only few studies showed microbial consumption of marine isoprene [Alvarez et al., 2009]. It is believed that the main loss of oceanic isoprene is emission to the atmosphere via air/sea gas exchange [Yokouchi et al., 1999; Palmer and Shaw, 2005; Meskhidze and Nenes, 2006].

The aim of this study was to investigate the surface ocean distribution of two important precursors of marine aerosols (i.e., DMS and isoprene) of similar biological origin and the influence of the biological setting on the distribution in different oceanic regions covering a broad range of productivity regimes. Although both DMS and isoprene have also abiotic sources and/or sinks, we focus in this study on their known common biogenic controls. Thus, simultaneous high-resolution measurements of dissolved DMS and isoprene concentrations in the surface ocean were conducted in the eastern Atlantic Ocean during the transit ANT-XXV/1 with R/V *Polarstern* from Bremerhaven, Germany, to Cape Town, South Africa, in November 2008 [Koch and Kattner, 2012]. In order to determine the environmental settings that may determine the distributions of DMS and isoprene, several parameters such as DMSP, phytoplankton and bacteria composition, nutrients, in situ chlorophyll *a* (Chl *a*), and satellite data of Chl *a* and calcite as well as the occurrence of eddy structures along the cruise track were examined. We identified nutrients as a possible general proxy that can be used to predict the relationship between DMS and isoprene distributions in nitrogen-depleted regions over the entire eastern Atlantic Ocean.

2. Methods

2.1. Trace Gas and DMSP Measurements

DMS and isoprene were continuously measured using an atmospheric pressure chemical ionization mass spectrometer (mini-CIMS), which consists of a ^{63}Ni atmospheric pressure ionization source coupled to a single quadrupole mass analyzer (Stanford Research Systems, SRS RGA200) [Saltzman *et al.*, 2009]. The mini-CIMS was coupled to a homemade porous Teflon membrane equilibrator. Seawater was pumped from approximately 2 m depth using a continuous pumping system off the side of the ship [Neogi *et al.*, 2011] and flowed at approximately 1 L min^{-1} through the equilibrator. A counterflow of dry, purified air (Dominick Hunter) was directed through the equilibrator at 100 mL min^{-1} . The equilibrated air stream was diluted with 1.7 L min^{-1} of clean purified air. Trideuterated DMS (CD_3SCH_3 , 2.78 ppm, 2 mL min^{-1}) was added to the air stream as an internal standard. Isoprene sensitivities were calculated by adding unlabeled isoprene from a standard tank to the equilibrated air stream every 12 h. The instrument sensitivity was 1.5×10^{-16} and $3.7 \times 10^{-16}\text{ A ppb}^{-1}$ for DMS and isoprene, respectively (where A is the signal current). One ppb corresponds to approximately 0.5 nM and 13 pM at 25°C for DMS and isoprene, respectively. Blanks and standards were measured for 30 min, followed by 12 h of continuous seawater measurements. This measurement protocol was repeated continuously. Measurements were removed from the data set when the seawater pumping system was not operating properly. We calculated the DMS concentrations by determining the equilibrated mixing ratio using the continuously monitored isotope standard and then applying the temperature-dependent Henry's law constant [Dacey *et al.*, 1984] using in situ measured sea surface temperature [Marandino *et al.*, 2007]. For isoprene in seawater, no temperature-dependent Henry's law (H) equation exists. Isoprene equilibration mixing ratios were calculated using the instrument isoprene sensitivity determined by standard addition. Seawater concentrations were computed using the freshwater temperature dependence from Mackay and Shiu [1981] and reduced by 10% to account for the salting-out effect. Because isoprene has a low solubility, a significant fraction of seawater concentration was transferred to the air flow in the equilibrator (roughly 35%). We corrected the measured seawater isoprene concentration to account for this effect. All data shown here are 5 min averages. The precision for DMS and isoprene measurements, calculated using the standard gases, were $\pm 6\%$ and $\pm 13\%$, respectively.

DMSP was measured using a gas chromatograph-flame photometric detection system [Zindler *et al.*, 2013]. The mean analytical errors of dissolved DMSP (DMSP_d), particulate DMSP (DMSP_p), and total DMSP (DMSP_t) were $\pm 19\%$, $\pm 20\%$, and $\pm 20\%$, respectively. Discrete samples were taken from the continuous seawater pumping system in time steps between 1 and 9 h. During the cruise, low temperatures in the laboratory caused problems with the detection limit, resulting in a period with missing DMSP data.

2.3. Additional Parameters

Phytoplankton pigment data from the transit are described in Taylor *et al.* [2011], and the nutrient data are described in Neogi *et al.* [2011] and Koch and Kattner [2012]. Moderate Resolution Imaging Spectroradiometer (MODIS) chlorophyll satellite data (<http://modis.gsfc.nasa.gov/>; 8 day composites) were used for each week of the cruise track, 4 weeks in total. A general introduction to the hydrographic and biogeochemical setting of the eastern Atlantic Ocean during the transit ANT-XXV/1 is given in Koch and Kattner [2012].

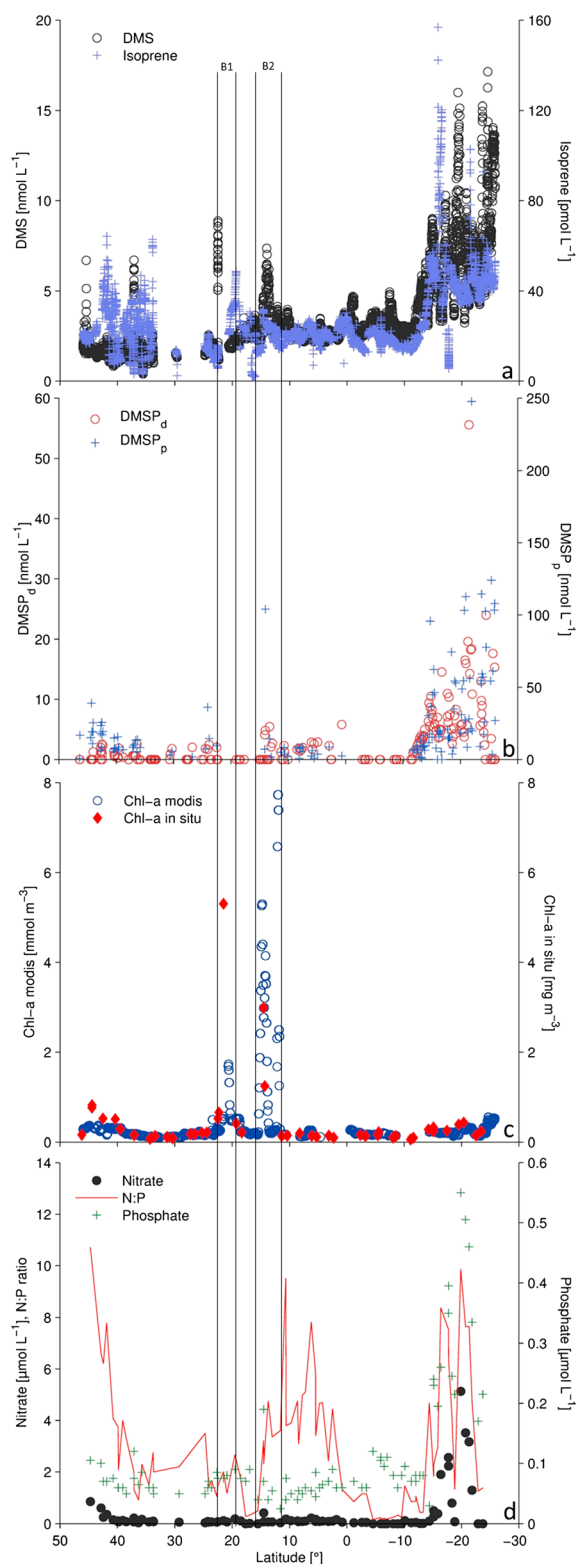


Figure 1. Distribution patterns of DMS, isoprene, DMSP (d = dissolved and p = particulate), Chl *a*, calcite, nitrate, phosphate, and the nitrogen to phosphate ratio (N:P) against latitude along the north-south transit in the eastern Atlantic Ocean. B1 and B2 show the position of two phytoplankton blooms.

2.4. Identification of Eddy Structures

The satellite-based Sea Level Anomaly (SLA) was examined to identify eddies along the cruise track. The delayed time-referenced SLA data set is provided by Archiving, Validation, and Interpretation of Satellite Oceanographic data at <http://www.aviso.oceanobs.com/>. Eddy-like structures are detected by an algorithm based on the Okubo-Weiß Method [Okubo, 1970; Weiss, 1991; Chelton *et al.*, 2007].

3. Results and Discussion

3.1. DMS, DMSP, and Isoprene Distribution Patterns

The mean DMS concentration was $3.6 \pm 1.2 \text{ nmol L}^{-1}$, which is comparable with the mean DMS concentration from the eastern Atlantic Ocean of $2.64 \pm 2.48 \text{ nmol L}^{-1}$ (Global Surface Seawater DMS Database: <http://saga.pmel.noaa.gov/dms>). DMS concentrations were generally between 1 and 4 nmol L^{-1} , except for two small peaks within phytoplankton blooms of up to 9 nmol L^{-1} between 19°N and 22°N (B1) and 11°N and 15°N (B2) [Taylor *et al.*, 2011] (Figure 1a). The overall DMS distribution is characteristic for this time of the year, with lower concentrations during fall/winter in the Northern Hemisphere and enhanced concentrations in spring/summer in the Southern Hemisphere [Lana *et al.*, 2011]. The distribution pattern of DMSP_d and DMSP_p followed roughly the distribution of DMS (Figure 1b). A mean isoprene concentration of $25.7 \pm 14.7 \text{ pmol L}^{-1}$ was measured along the entire transit. Isoprene concentrations measured in this study are in the range of previous studies in the Atlantic Ocean and North Sea ($0.1\text{--}100 \text{ pmol L}^{-1}$) [Milne *et al.*, 1995; Broadgate *et al.*, 1997; Baker *et al.*, 2000]. Comparable to DMS, isoprene concentrations were higher in the Southern Hemisphere.

3.2. The Influence of the N:P Ratio on the DMS, DMSP, and Isoprene Relationship

Despite the fact that Chl *a* (both satellite and in situ data, Figure 1c) and other phytoplankton pigments were neither correlated with DMS nor with isoprene along the cruise track of this study, both compounds may have similar biogenic sources and/or sinks [Keller *et al.*, 1989; Shaw *et al.*, 2010]. The lack of correlations with pigment data may reflect the fact that

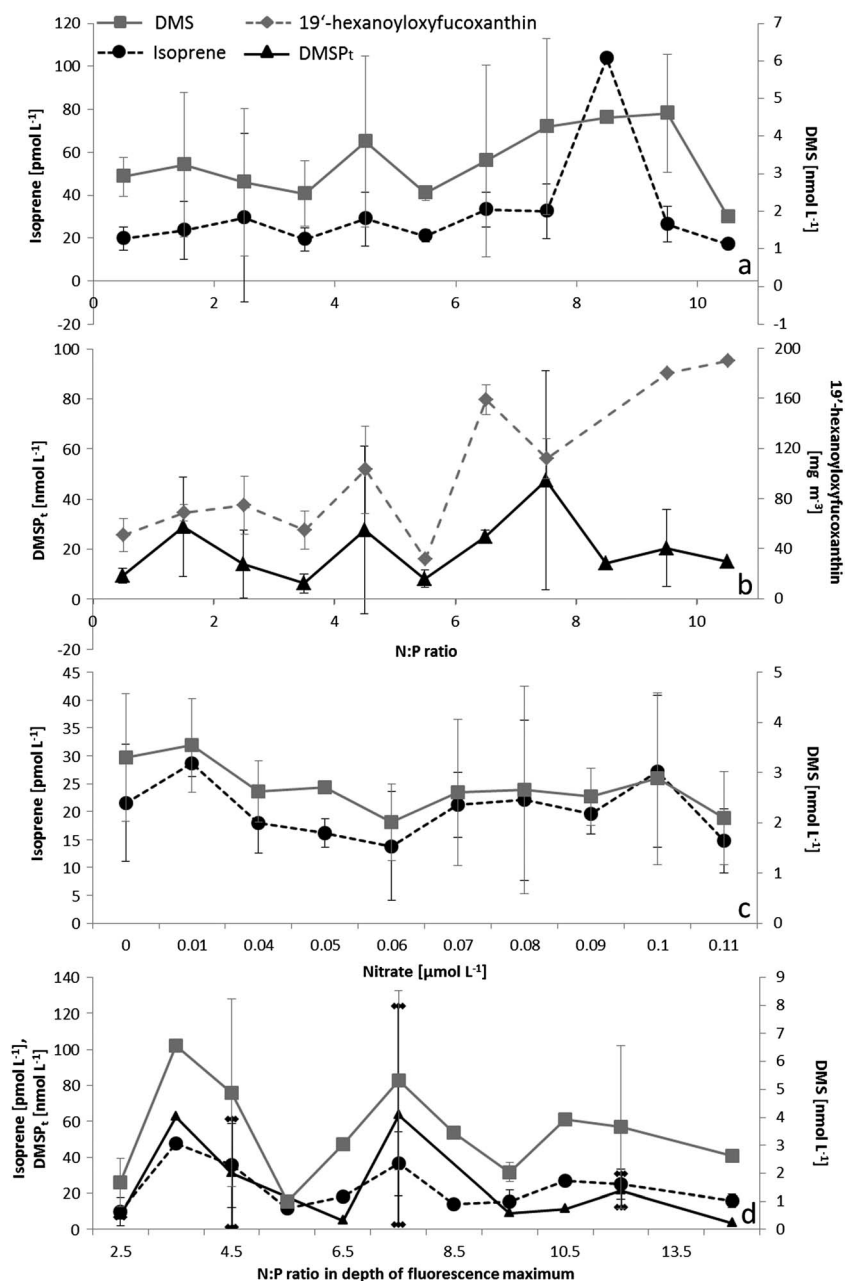


Figure 2. (a, b) Binned data of isoprene, DMS and DMSP_t and 19'-hexanoyloxyfucoxanthin for different N:P ratios in surface seawater. (c) DMS and isoprene data binned for different nitrate concentrations in surface seawater. (d) Surface seawater DMS and isoprene data binned for different N:P ratios in the depth of fluorescence maximum between 24 and 105 m. The error bars indicate the standard deviations of the means of each bin. Thick ends of error bars clarify the length of the error bars of DMSP_t in Figure 2d.

pigments only constitute one proxy of trace gas sources, namely phytoplankton, and neglect the role of bacteria as a source or sink. The availability of nutrients is essential to sustain phytoplankton and bacteria communities. Thus, we investigated the influence of phytoplankton and bacterioplankton on the isoprene, DMS, and DMSP distributions, indirectly, by clustering the data dependent on the N:P ratio (nitrogen (N) to phosphate (P) ratio, where N is the sum of nitrate, nitrite, and ammonia): We calculated the average of the DMS, the DMSP_t, and the isoprene concentrations over the entire transit for bins of N:P ratios (e.g., the N:P ratio of 2 to 3 was allocated to a N:P bin of 2.5) according to Zindler *et al.* [2012] (Figure 2). Between 1 and

17 data points of sulfur and isoprene were averaged per bin. Figure 1d shows an overview of the nutrient distribution along the transit.

Isoprene and DMSP_t peaked at the N:P bin of 7.5, while DMS peaked in the N:P bin of 8.5 (Figure 2). We correlated the binned values of DMS, DMSP_t , and isoprene of all N:P bins with each other. All three compounds showed significant correlations in the N:P range of 0 to 8 (DMS versus isoprene: Pearson's coefficient of determination (R^2) = 0.52, p value 0.05; DMSP_t versus DMS: R^2 = 0.88, p value 0.001; isoprene versus DMSP_t : R^2 = 0.53, p value 0.05; for all n = 8). The close link between DMS and DMSP_t is well known [Vogt and Liss, 2009]. However, to our understanding, the correlations between seawater isoprene and the sulfur compounds have not been previously reported. The correlations imply common pathways, such as production and consumption by similar phytoplankton and bacteria groups, dependent on the nutrient availability. And indeed, the binned data of the phytoplankton pigment 19'-hexanoyloxyfucoxanthin (19'-hex), a diagnostic pigment for haptophytes and dinoflagellates (A. Bracher, personal communication, 2014), correlated significantly with isoprene (R^2 = 0.77, p value 0.01, n = 8), DMS (R^2 = 0.85, p value 0.01, n = 7) and DMSP_t (R^2 = 0.74, p value 0.05, n = 7), respectively, in the N:P range of 0 to 8. Haptophytes and dinoflagellates include important DMSP producing algae species, with some species also identified as isoprene producers [Keller et al., 1989; Shaw et al., 2010]. No correlations were observed for N:P > 8. It might be possible that in regions of elevated nitrogen (N:P > 8) production/consumption pathways are dominated by other bacteria and phytoplankton groups leading to a decoupling of isoprene and DMS/DMSP pathways. This assumption is supported by the fact that isoprene, DMS, DMSP_t , and 19'-hex are not significantly correlated among each other when all N:P bins (0.5–9.5) were considered. These poor correlations were caused by the different distribution pattern of isoprene, DMS, DMSP_t , and 19'-hex within the N:P bins of 8.5 and 9.5.

In addition, DMS and isoprene were also correlated significantly (R^2 = 0.66, p value 0.01, n = 10) in regions of low nitrate concentrations ($<0.11 \mu\text{mol L}^{-1}$) when they were clustered against the nitrate concentrations in steps of $0.01 \mu\text{mol L}^{-1}$ (Figure 2c). We determined that the N:P ratios were not controlled by nitrate concentrations. Therefore, the nitrate correlation provides additional information about the link between DMS and isoprene, which shows that they largely depend on nutrient availability.

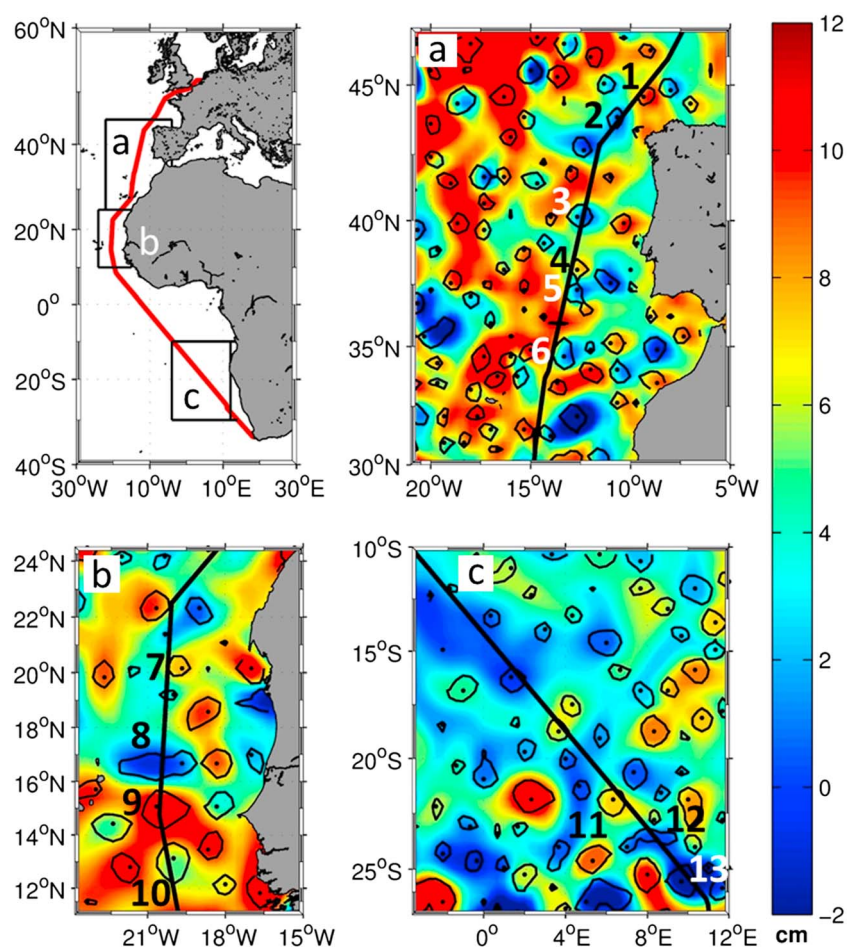
Furthermore, we clustered DMS, isoprene, DMSP_t , and different phytoplankton pigments against the N:P bins in the same way as described above, but using nutrient values from the fluorescence maximum depths, which were located between 24 and 105 m during the transit. Significant correlations between DMS and isoprene (R^2 = 0.81, p value 0.001, n = 11), DMS and DMSP_t (R^2 = 0.62, p value 0.01, n = 9), and between isoprene and DMSP_t (Spearman's rank correlation coefficient (r_s) = 0.83, p value 0.01, n = 10; r_s is used here due to lack of normally distributed data) were found, confirming again the close link between these compounds. Additionally, DMS and isoprene also correlated significantly (R^2 = 0.62, p value 0.01, n = 8) when they were clustered against the nitrate concentrations from the fluorescence maximum depths as described above. The correlations were found for the entire nutrient range (N:P up to 15 and nitrate up to $8.3 \mu\text{mol L}^{-1}$); however, no correlations were found between the pigments and isoprene, DMS, or DMSP_t . Thus, we assume that nutrients regulated all biological activities, not only those related to phytoplankton, in the fluorescence maximum, which in turn can also determine the relationship between DMS and isoprene in surface seawater. However, we cannot explain at this time the reason for the correlations between DMS, DMSP_t , and isoprene when they were clustered by nutrients from the fluorescence maximum depth. Nonetheless, the result that these correlations were partly higher than the correlations found in the surface ocean is intriguing.

3.3. The Influence of Eddies on DMS and Isoprene

Nonlinear mesoscale features of the oceanic circulation, so-called eddies, play an important role for the horizontal transport and vertical distribution of nutrients in both open ocean and coastal regions. Eddies can generate quasi-enclosed mesoscale environments that possess characteristics (e.g., phytoplankton community and nutrient distribution) distinct from the surrounding open ocean. Three types of eddies have been identified: cyclonic, anticyclonic, and mode water eddies [McGillicuddy et al., 2007]. Both mode water eddies (MWE) and anticyclonic eddies (ACE) have a clockwise rotation in contrast to counterclockwise rotation in cyclonic eddies (CE) on the Northern Hemisphere. Both CE and MWE can inject nutrients from below the euphotic zone into the euphotic zone during their early stages, while ACE tend to decrease the nutrient content of the euphotic zone. Thus, eddy-driven pumping of nutrients into the euphotic zone by CE

Table 1. Eddies (ACE = Anticyclonic Eddies, CE = Cyclonic Eddies) Passed Along the North South Transit in the Eastern Atlantic Ocean and Ancillary Data Taken Within the Eddies^a

Eddy	Latitude	r_s DMS Versus Isoprene	Nitrate ($\mu\text{mol L}^{-1}$)	Phosphate ($\mu\text{mol L}^{-1}$)	N:P	Chl <i>a</i> (mg m^{-3})	Diatoms ($\mu\text{g L}^{-1}$)
1 ACE	45°N	0.3	0.7	0.1	9.2	0.76	0
2 CE	43°N	0.3	0.6	0.1	6.6	n. d.	0
3 CE	40°N	0.96	0.09	0.06	2.9	0.29	0
4 ACE	38°N	0.74	0.08	0.05	3.3	n. d.	n. d.
5 CE	37°N	0.2	0.15	0.1	1.7	0.15	0.006
6 CE	34°N	0.56	0.07	0.06	1.5	0.07	0
7 ACE	20°N	0.32	0.13	0.09	1.9	0.4	n. d.
8 CE	17°N	0.86^b	0.01	0.09	0.3	n. d.	n. d.
9 ACE	15°N	0.8	0.1	0.09	2.7	2.9	1.87
10 CE	13°N	0.5	0.07	0.06	3.4	n. d.	n. d.
11 ACE	21°S	0.09	2.3	0.5	7.6	n. d.	n. d.
12 CE	23°S	0.32	0	0.17	1.3	0.15	0
13 CE	25°S	0.01	n. d.	n. d.	n. d.	n. d.	n. d.

^aSpearman's correlation coefficient is r_s ; significant correlations are given in bold; n. d.: no data.^bAnticorrelation.**Figure 3.** (top, left) Cruise track of the north-south transit of ANT-XXV/1 in the eastern Atlantic Ocean (red line) is separated into (a) north, (b) middle, and (c) south regions (boxes). In Figures 3a–3c, sea level anomalies detected by satellite (indicated by colors) show the distribution of eddies within the boxes (Figure 3a) snapshot from 9 November 2011, (Figure 3b) snapshot from 14 November 2011, and (Figure 3c) snapshot from 26 November 2011. The black thick line shows the cruise track. Black dots show the center of the eddies. The black circles show the calculated position of the eddies using the algorithms described in section 2.3. Numbers 1–13 indicate the eddies, which were described in Table 1. Eddies between 34°N and 25°N could not be considered because of missing DMS and isoprene data. No eddies could be determined between 10°N and 10°S.

and MWE fuel the primary production of phytoplankton in oligotrophic and eutrophic regions [McGillicuddy *et al.*, 2007; Stramma *et al.*, 2013].

Based on our high-resolution measurements of DMS and isoprene, we could investigate in more detail the DMS and isoprene distributions within eddies passed through along the cruise track. In 6 out of 13 identified eddies (located at 40°N, 38°N, 34°N, 17°N, 15°N, and 13°N), we found significant correlations between DMS and isoprene (Table 1 and Figure 3). All correlations were found for eddies with low N:P (<3.4) and low nitrate concentrations (<0.1 $\mu\text{mol L}^{-1}$). In contrast, eddies showing no correlations between DMS and isoprene had higher nitrate concentrations except for eddy # 12. This influence of low nitrate is in agreement with our findings in section 3.2. Within the CE #3 at 40°N and in the ACE #9 at 15°N, the highest correlation coefficients of DMS versus isoprene were determined ($r_s = 0.96$, $n = 70$; $r_s = 0.8$, $n = 76$, respectively, p value 0.01). Both eddies showed a similar N:P ratio of ~2.8. Conversely, within the nitrate depleted CE #8 (with a N:P ratio of 0.3), a significant anticorrelation between DMS and isoprene was observed. CE #8 at 17°N as well as the ACE #9 at 15°N were most likely generated in coastal regions off Mauritania and Senegal and moved westward to the region of the cruise track within 3 months [Schütte, 2013]. Both eddies were likely initially enriched with comparable nutrient concentrations because of their coastal origin. However, the nutrient concentration, phytoplankton community, and DMS/isoprene relationship appeared to have evolved differently since the time of their formation. This discrepancy might be explained when ACE #9 is identified as a MWE characterized by high Chl *a* concentrations associated with a dominance of diatoms [McGillicuddy *et al.*, 2007]. In comparison to a CE with low biomass and productivity during its later stage, a mode water eddy of the same age can show long-lasting diatom blooms [McGillicuddy *et al.*, 2007]. Indeed, ACE #9 showed the highest concentrations of both Chl *a* (2.9 mg m^{-3}) and diatoms (1.87 $\mu\text{g L}^{-1}$) of all identified eddies along the cruise track, although the eddy was persistent. Nitrate depletion in CE #8 most probably led to the termination of the phytoplankton bloom, which in turn may have promoted the development of bacterioplankton, such as bacteria of the genus *Rhodobacteraceae*, which was found frequently along the transit [Friedline *et al.*, 2012]. It seemed that *Rhodobacteraceae* can consume isoprene [Alvarez *et al.*, 2009] while concurrently producing DMS [Curson *et al.*, 2008]. Thus, we speculate that the DMS/isoprene anticorrelation found for CE #8 might have been caused by bacterial activities. However, the role of bacteria for the DMS/isoprene distribution in the ocean needs to be further investigated.

4. Conclusions

High-resolution measurement of dissolved DMS and isoprene in the surface ocean during a north-south transit in the eastern Atlantic Ocean revealed a significant correlation of DMS and isoprene in regions with N:P ratio <8 (i.e., nutrient-depleted regions). Additionally, a significant correlation between DMS and isoprene was found in regions with low nitrate concentrations (<0.11 $\mu\text{mol L}^{-1}$). Algae groups containing 19'-hex, including haptophytes and dinoflagellates, were identified as a potential source of both DMS and isoprene in the nitrogen-depleted regions (N:P <8). Furthermore, significant positive correlations between DMS and isoprene were found in mesoscale eddies with N:P ratios <3.4 and nitrate concentrations <0.1 $\mu\text{mol L}^{-1}$, whereas an extremely nitrate (0.01 $\mu\text{mol L}^{-1}$) depleted eddy (N:P = 0.3) showed a significant anticorrelation of DMS and isoprene.

We conclude that although nutrients have no direct influence on the DMS and isoprene concentrations, the low-nutrient regime seem to favor a common pathway for both DMS and isoprene, such as production by 19'-hex-containing algae. DMS and isoprene pathways are characterized by a complex interplay of certain phytoplankton and bacteria groups, which are sensitive to changes in the concentration and composition of nutrients. Thus, nutrient concentrations might be a more suitable indicator for detecting links between DMS and isoprene, rather than phytoplankton pigments like Chl *a*. This is supported additionally by the absence of any correlations of isoprene or DMS with phytoplankton pigments along the cruise track. Although we showed a clear linkage between DMS and isoprene pathways, the mechanism behind this relationship remains to be investigated. Despite this uncertainty, we suggest that the relationship between DMS and isoprene clustered by N:P or nitrate has the potential to be used to predict the DMS or isoprene surface distribution: For instance, isoprene concentrations may be computed from N:P and DMS measurements in low-nutrient regions. To this end, we suggest to test the relationship with an extended data set covering additional oceanic regions with different settings.

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